

TIME EVOLUTION OF THE PULSED HF CHEMICAL LASER SYSTEM. II. IRREVERSIBLE THERMODYNAMIC ANALYSIS[‡]

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The time rates of change of level populations and radiation densities derived from a detailed kinetic model of the $F + H_2 \rightarrow HF + H$ laser are employed as input data for a time dependent thermodynamic analysis of this system. The laser is regarded as an irreversible heat engine generating thermodynamic work in the form of laser light. The development in time of the thermodynamic functions, efficiency and irreversible entropy production is determined by computing the contributions of pumping, radiation and relaxation to the entropy and energy of the lasing molecules. Effects of specific rate processes are evaluated by considering different kinetic schemes, i.e. different combinations of kinetic processes and initial conditions. It is shown, among others, that a laser without relaxation processes ("frictionless") has poor efficiency despite the absence of energy losses and the low irreversible entropy production. On the other hand, the efficiency is high in lasers governed by fast rotational relaxation. This is because rotational relaxation, though leading to some energy losses and irreversible entropy production, compensates for the entropy decrease of the system (while lasing under partially inverted populations) by increasing the bath entropy. The major general conclusion of the analysis is that the thermodynamic constraints related to the kinetic scheme and not the extent of irreversibility of the lasing process is the crucial factor in determining the laser efficiency.

I. Introduction

In electrochemical cells the chemical energy stored in a nonequilibrium chemical mixture is converted into electrical energy. Similarly, in chemical and other molecular lasers the energy stored in the nonequilibrium molecular populations generated by the pumping process is converted into laser radiation. Coherent laser radiation, like electrical current, carries energy but no (or negligible) entropy and is thus equivalent to thermodynamic work [1–4]. Hence a thermodynamic approach to chemical lasers can be, and has been, constructive for better understanding the behaviour of these complex nonequilibrium chemical

systems. For example, based on free energy considerations one can evaluate upper bounds to the laser efficiency for different initial and external conditions. Among others, it can be shown that the enhancement of the laser efficiency due to fast rotational relaxation results from removal of thermodynamic constraints on the molecular distribution function [5].

In previous works [6,7][‡] we have calculated upper bounds to the laser efficiency by regarding the lasing process as a sequence, or cycle, of equilibrium and quasi-equilibrium stages, e.g. the reactants, the nascent products of the pumping reaction, the partly (usually rotationally) relaxed pre-lasing populations, the post-lasing and the totally relaxed products [3]. From the energy and entropy changes in the various

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[‡] For a review, see ref. [7].

stages it is possible to find limits to the laser efficiency and the dissipative losses. This equilibrium thermodynamic type analysis provides insights into the mechanisms of energy storage and conversion in chemical lasers. Also, it is quite realistic in the sense that the various stages in the lasing cycle are usually well separated in time. Yet, the equilibrium thermodynamic approach has two inherent limitations, which are not specific to chemical laser systems. First, it provides no information on the temporal evolution of the thermodynamic functions during the passage from one state to another. Second, the upper bounds to the laser efficiencies derived from the time independent description might be far remote from the actual efficiencies. In other words, the laser is regarded as a reversible heat engine while actual chemical lasers are equivalent to irreversible heat engines.

In this paper we present a comprehensive time dependent thermodynamic analysis of a typical chemical laser system; the flash initiated $F + H_2 \rightarrow HF + H$ laser model described in the previous paper [8] (henceforth paper I). Some of the initial conditions examined in this model simulate the experimental conditions employed by Berry [9]. The results of the kinetic modeling will serve us as input data for the thermodynamic description. Based on the time rates of change of the level populations, photon densities, translational temperature and the nonlasing species concentrations obtained by solving the rate equations, and the statistical mechanical (information theoretic) definitions of entropy and energy of a nonequilibrium molecular system [7] we shall study the time evolution of the various thermodynamic characteristics of the laser system. The first and second law of thermodynamics will enable us to assess the irreversible entropy production and heat production in the system and the deviation of the instantaneous and integrated efficiencies from their ideal (reversible) values [10]. By comparing the relative instantaneous contributions to the entropy and energy of the system and the surrounding heat bath it will be possible to identify memory effects which reflect the mechanisms of energy storage and conversion in chemical lasers.

The thermodynamic information on the time evolution of the system appears latently among the very detailed microscopic data provided by the laser rate equations. The main virtue of the thermodynamic

analysis presented in the following is in processing and focusing the detailed kinetic data into a few macroscopically significant quantities. These quantities (e.g. the work and heat production) are interrelated by the basic laws of thermodynamics. Also, they are more feasible for experimental determination than the photon and molecular populations. In the present study the experimental system will be realized by the kinetic model described in paper I [8]. In the theoretical framework of this work the kinetic model has two advantages over a real experimental system. First, it is free from unknown factors and detection errors. Second, it allows to evaluate the specific thermodynamic effects of different kinetic processes which in real systems occur simultaneously. For example, in the kinetic modeling we found that rotational and vibrational relaxation play opposing roles in affecting the laser efficiency. Here we shall show that while in nonlasing mixtures both processes are dissipative, in lasing systems rotational relaxation reduces the irreversible entropy increase of the system by coupling the internal degrees of freedom of the lasing molecules to the heat bath. The heat transferred from the system to the bath due to this coupling leads to entropy increase of the bath which compensates for the entropy decrease of the system thereby allowing efficient extraction of energy from partially inverted vibrational populations[‡].

2. Thermodynamic background

The thermodynamic description of pulsed chemical laser systems presented in this work is based entirely on the first and second law of thermodynamics and the statistical mechanical, or information theoretic, definitions of entropy and energy in nonequilibrium molecular systems. In order to introduce the basic concepts and quantities required for the thermodynamic analysis and to emphasize the thermodynamic character of chemical lasers let us visualize these systems as continuous, non-cyclic and irreversible heat engines. The "working substance" in these heat engines are the internal degrees of freedom of the lasing molecules, which henceforth will be considered as the "system". The system is coupled

[‡] See for example, refs. [11].

simultaneously to two heat reservoirs. A "hot reservoir" represented by the reactants of the chemical pumping reaction supplies "heat", i.e. energy, E_p , and entropy, S_p , to the system; $E_p = E_p(t)$ and $\dot{S}_p = \dot{S}_p(t)$ are the total amounts of energy and entropy provided to the system by the pumping reaction in the time interval $t = 0$ to t . The rates of energy and entropy pumping, \dot{E}_p and \dot{S}_p respectively, are proportional to the rate of the pumping reaction, see below. (An effective, constant, pumping temperature $T_p = \dot{E}_p/\dot{S}_p$ can be associated with the "hot reservoir".) A part of the pumped energy is converted into thermodynamic work, W , (laser output) and another part, Q , is delivered to a "cold reservoir" comprising all the non-lasing species and the translational degrees of freedom of the lasing molecules; $Q = Q(t)$ and $W = W(t)$ are, respectively, the total heat released into the cold reservoir and the total laser energy between $t = 0$ and t . In the following we shall refer to the cold reservoir as the "heat bath". The heat bath is assumed to be in internal equilibrium, characterized by a well defined temperature T throughout the lasing. Yet, since its heat capacity is finite, the temperature $T = T(t)$ may be time dependent. The rate of work production, or equivalently, the instantaneous laser output power, \dot{W} , is determined by the rates of stimulated radiation processes taking place in the laser cavity. Similarly, \dot{Q} , the rate of heat transfer from the system to the bath is determined by the relaxation processes. Correspondingly, the rate at which the bath entropy increases is $\dot{S}_b = \dot{Q}/T$, where $T = T(t)$ is the instantaneous bath temperature. It should be emphasized that \dot{S}_b represents only the system's contribution to the bath entropy. It does not account for all the entropy changes of the bath. For example, the pumping reaction releases part of its exoergicity into the translational degrees of freedom of the product molecules which according to our definition, belong to the heat bath rather than to the system. This leads to direct contributions of energy and entropy from the hot reservoir into the heat bath which are not included in \dot{Q} and \dot{S}_b . Other processes, not involving the internal degrees of freedom of the lasing molecules such as secondary chemical reactions or the residual flash energy provide other direct contributions to the thermodynamic functions of the heat bath which influence, of course, its temperature T . Similarly, the quantities \dot{E}_p and

\dot{S}_p introduced above incorporate only the direct contributions of the pumping reaction to the energy and entropy of the internal degrees of freedom of the HF molecules.

In pulsed chemical lasers the energy, $E = E(t)$, and the entropy, $S = S(t)$, of the system, i.e. the total energy and entropy contents of the internal degrees of freedom of the lasing molecules are time dependent. This is due to two factors: First, N , the absolute number of lasing molecules (per unit volume) increases in time; $\dot{N} \geq 0$. Second, the internal energy distributions are changing due to the radiative and nonradiative processes. The time rate of change of the system energy, \dot{E} , is related to \dot{E}_p , \dot{Q} and \dot{W} by the first law of thermodynamics, which expresses the energy balance in the laser system [10]. Namely,

$$\dot{E} = \dot{E}_p - \dot{W} - \dot{Q}. \quad (1)$$

At $t = 0$, the time of initiating the pumping process, $N = 0$ and consequently $E(t = 0) = E_p(t = 0) = 0$. Hence, integration of (1) yields

$$E = E_p - W - Q, \quad (2)$$

where $E = E(t)$ is the instantaneous internal energy and E_p , W and Q are the integrated quantities defined above. Using X to denote any of these quantities as well as the entropies S_p , S_b and S , which all satisfy $S(t = 0) = 0$, we have, of course

$$X = X(t) = \int_0^t \dot{X}(t') dt'. \quad (3)$$

The second law of thermodynamics implies that for any infinitesimal change in the state of the systems, $dS \geq \sum dS_i = \sum dQ_i/T_i$, where dS_i and dQ_i are the entropy and heat exchange with reservoir i governed by temperature T_i , respectively. In our case we have two such reservoirs whose respective contributions to the sum are $dE_p/T_p = dS_p$ and $-dQ/T = -dS_b$. Consequently,

$$\dot{S} \geq \dot{S}_p - \dot{S}_b = \dot{S}_p - \dot{Q}/T, \quad (4)$$

with equality for reversible operation.

Integration of (4) yields

$$S \geq S_p - S_b = S_p - \int_0^t \dot{Q}(t')/T(t') dt'. \quad (5)$$

The difference

$$\dot{S}_{\text{ir}} \equiv \dot{S} + \dot{S}_{\text{b}} - \dot{S}_{\text{p}}, \quad (6)$$

represents the rate of irreversible entropy production (in the "universe"). Similarly

$$S_{\text{ir}} = S + S_{\text{b}} - S_{\text{p}}, \quad (7)$$

is the integrated irreversible entropy production. A reversible process is defined as a process in which \dot{S}_{ir} (and hence also S_{ir}) is identically zero. The efficiency of heat engines based on "working fluids" in internal equilibrium is improved by reducing the irreversible entropy production (during the contact with the heat reservoirs). However, in chemical lasers the working fluid comprising the internal degrees of freedom is not in internal equilibrium. Consequently, $\dot{S}_{\text{ir}} > 0$ may be due to a variety of processes, some of which occurring within the working fluid. As we shall see below, among these processes there are some, which though leading to a certain irreversible entropy production and, correspondingly, to dissipation of energy, play a major role in enhancing the laser efficiency.

All the thermodynamic equalities can be applied to cw lasers. In fact, the appropriate expressions for cw systems are considerably simpler. Here E and S should refer to the internal energy and entropy of the lasing molecules present at any moment in the laser cavity. Since cw systems are in steady state the concentration of the lasing (and all other) molecules as well as their internal energy distribution are time independent. Hence $\dot{E} = 0$ and $\dot{S} = 0$. Since all energy and entropy fluxes into and out of the cavity are constant, the quantities \dot{E}_{p} , \dot{S}_{p} , \dot{Q} , \dot{S}_{b} , \dot{S}_{ir} and T are constants. Thus, for example, eqs. (1) and (6) reduce to

$$0 = \dot{E}_{\text{p}} - \dot{W} - \dot{Q} \quad (\text{cw}), \quad (8)$$

$$\dot{S}_{\text{ir}} = \dot{S}_{\text{b}} - \dot{S}_{\text{p}} \quad (\text{cw}). \quad (9)$$

Upper bounds to the laser efficiency can be derived by combining the results of the first and second law. Before doing so we shall introduce the explicit expressions for the thermodynamic functions of chemical lasers. Using E_{vJ} to denote the energy of the vib-rotational level v, J ; N_{vJ} for the number of molecules (per unit volume) in this level at time t and $P(v, J) = N_{vJ}/N = N_{vJ}/\sum N_{vJ}$ for the normalized vib-rotational distribution at time t we have

$$E = \sum_{v,J} N_{vJ} E_{vJ} = N \sum_{v,J} P(v, J) E_{vJ} = N\langle e \rangle, \quad (10)$$

where $\langle e \rangle$ is the average internal energy per molecule. Note that E is the internal energy per unit volume of the laser cavity (i.e. E is in units of cal/cm³). All other extensive functions introduced below, such as E_{p} , S or W also refer to unit volume of the laser cavity.

The time rate of change of E is

$$\begin{aligned} \dot{E} &= \sum \dot{N}_{vJ} E_{vJ} = \dot{N} \sum_{v,J} P(v, J) E_{vJ} + N \sum_{v,J} \dot{P}(v, J) E_{vJ} \\ &= \dot{N}\langle e \rangle + N\langle \dot{e} \rangle. \end{aligned} \quad (11)$$

The entropy stored in the internal degrees of freedom of the laser active molecules is [5-7]

$$\begin{aligned} S &= -k \sum_{v,J} N_{vJ} \ln [N_{vJ}/(2J+1)N] \\ &= -kN \sum_{v,J} P(v, J) \ln [P(v, J)/(2J+1)] = N\langle s \rangle, \end{aligned} \quad (12)$$

where k is the Boltzmann constant and $\langle s \rangle$ is the average internal entropy per molecule.

The time rate of change of S is given by

$$\begin{aligned} \dot{S} &= -k\dot{N} \sum P(v, J) \ln [P(v, J)/(2J+1)] \\ &\quad - kN \sum \dot{P}(v, J) \ln [P(v, J)/(2J+1)] = \dot{N}\langle \dot{s} \rangle + N\langle \dot{s} \rangle. \end{aligned} \quad (13)$$

Energy and entropy are pumped into the system by the pumping reaction [9]



The (negligibly slow) reverse reaction will not be taken into account in our analysis. The rate of pumping energy and entropy into the internal degrees of freedom of the HF molecules are

$$\begin{aligned} \dot{E}_{\text{p}} &= \sum_{v,J} k(v, J) [\text{F}] [\text{H}_2] E_{vJ} = \dot{N} \sum_{v,J} P_i(v, J) E_{vJ} \\ &= \dot{N}\langle \epsilon_{\text{p}} \rangle, \end{aligned} \quad (15)$$

$$\dot{S}_{\text{p}} = -k\dot{N} \sum_{v,J} P_i(v, J) \ln [P_i(v, J)/(2J+1)] = \dot{N}\langle s_{\text{p}} \rangle. \quad (16)$$

Here $k(v, J)$ is the rate constant of (14), $P_i(v, J) = k(v, J)/\sum k(v, J)$ is the vib-rotational distribution of

the nascent HF molecules, $\langle \epsilon_p \rangle$ and $\langle s_p \rangle$ are the average internal energy and entropy per molecule of nascent HF, respectively. Integration of (15) and (16) yields

$$E_p = N \sum_{v,J} P_i(v,J) E_{v,J} = N \langle \epsilon_p \rangle, \quad (17)$$

$$S_p = -Nk \sum_{v,J} P_i(v,J) \ln [P_i(v,J)/(2J+1)] = N \langle s_p \rangle. \quad (18)$$

The rate of extracting thermodynamic work from the system (per unit laser active volume) is the net rate of stimulated emission [8], i.e.

$$\dot{W} = c \sum_{v,J} \sigma_{v,J} \Delta N_{v,J} \rho_{v,J} = \sum_{v,J} (\dot{\rho}_{v,J} + \rho_{v,J}/\tau_p) = \dot{\rho} + \rho/\tau_p, \quad (19)$$

where c is the light velocity and τ_p is the photon lifetime in the cavity. $\sigma_{v,J}$, $\Delta N_{v,J}$ and $\rho_{v,J}$ are the cross section for stimulated emission, the population inversion and the radiation density in the $v, J-1 \rightarrow v-1, J$ transition, respectively. $\rho_{v,J} = h\nu_{v,J} \phi_{v,J}$, where $\phi_{v,J}$ is the photon density and $\nu_{v,J}$ the transition frequency. It should be noted that \dot{W} is the rate of stimulated emission in the cavity. The rate of output coupling from the laser is given by the second term in (19), ρ/τ_p . Since the stimulated emission tends to reduce $\Delta N_{v,J}$ to $\Delta N_{v,J}^{\text{th}}$ which implies $\dot{\rho} = 0$ the second term in (19) is generally much larger than the first term. It is identically zero for cw lasers and set equal to zero in the steady state ("gain equal loss") approximation of pulsed systems [12,13].

The total laser energy between $t = 0$ and t is

$$W(t) = \rho(t) + \frac{1}{\tau_p} \int_0^t \rho(t') dt'. \quad (20)$$

The total pulse energy is obtained from (20) by setting $t > t_q$ where t_q is the pulse quenching time. Since $\rho(t > t_q) = 0$ only the second term in (20) contributes to $W = W(t > t_q)$.

The rate of heat transfer from the system to the bath, \dot{Q} , can be determined from $\dot{Q} = \sum X_i q_i$, where X_i is the rate of the relaxation process i and q_i is the heat released in this process. However, in the computations presented below \dot{E} , \dot{E}_p and \dot{W} were determined from (11), (15) and (19), respectively, and \dot{Q} from (1). Similarly Q was evaluated from (2). The corresponding contributions to the bath entropy were computed as $\dot{S}_b = \dot{Q}/T$ and $S_b = \int_0^t \dot{S}_b dt' = \int_0^t \dot{Q}(t')/$

$T(t') dt'$, cf. eqs. (4) and (5). Finally, \dot{S}_{ir} and S_{ir} were computed via (6) and (7), respectively.

The input data required for the thermodynamic analysis are $N(v, J)$, $\rho_{v,J}$ (or $\phi_{v,J}$) and T . All these quantities have been determined by solving the laser rate equations for the kinetic model of the HF laser described in the previous paper [8].

Combination of (1) and (4) yields a theoretical upper bound to the instantaneous laser power [10], i.e.

$$\dot{W} \leq (\dot{E}_p - T\dot{S}_p) - (\dot{E} - T\dot{S}). \quad (21)$$

This inequality can be re-expressed in terms of the Helmholtz free energy of the system $A = E - TS$ and the pumping contribution to the free energy defined as, $A_p = E_p - TS_p$;

$$\dot{W} \leq (\dot{A}_p - \dot{T}S_p) - (\dot{A} - \dot{T}S). \quad (22)$$

If the heat bath is infinite so that $T = \text{const.}$ eq. (22) reduces to [10]

$$\dot{W} \leq \dot{A}_p - \dot{A}. \quad (23)$$

For cw lasers where $\dot{S} = \dot{E} = 0$ and $T = \text{const.}$ eq. (22) is further reduced, i.e.

$$\dot{W} \leq \dot{A}_p = \dot{E}_p - T\dot{S}_p \quad (\text{cw}). \quad (24)$$

Upper bounds to the integrated laser energy, $W(t)$, are obtained by integrating eqs. (21)–(24). Thus, in the general case where T is time dependent we find from (21)

$$W \leq (E_p - E) - \int_0^t T(\dot{S}_p - \dot{S}) dt'. \quad (25)$$

For $T = \text{const.}$ we get from (23)

$$W \leq A_p - A = (E_p - E) - T(S_p - S). \quad (26)$$

Finally, for cw lasers (24) yields

$$W \leq A_p \quad (\text{cw}). \quad (27)$$

The bounds on \dot{W} and W can be transformed into bounds on the laser efficiency. We shall use two kinds of efficiencies to characterize the laser performance. The instantaneous efficiency

$$\chi = \chi(t) = \dot{W}/\dot{E}_p \quad (28)$$

and the integrated efficiency

$$\eta = \eta(t) = W/E_p. \quad (29)$$

The instantaneous efficiency provides a quantitative measure for the mechanism of energy storage and conversion in the laser system [10]. In a system with "memory" the energy supplied by the pumping process can be stored in the internal degrees of freedom of the lasing molecules without being immediately released as heat or radiation. As long as internal energy is accumulated $\dot{E} > 0$ while \dot{W} and χ are small. Then, if this energy is suddenly liberated as a pulse of laser radiation, \dot{E} is typically largely negative and \dot{W} and χ may reach very high values. Later on we shall see that in certain cases χ may largely exceed unity. This behaviour is typical to Q -switched lasers [13]. Oscillations in χ are also expected at the lasing threshold region (relaxation oscillations). In "memoryless" systems, e.g. cw lasers, the energy pumped into the system is immediately converted to radiation and heat. In this case χ is constant. It can be anticipated that a similar behaviour (i.e. slowly varying χ) will be observed in the near steady state region which usually characterizes the second (post-threshold) lasing period in pulsed chemical lasers.

Combining (21) and (28) we find

$$\chi \leq 1 - \dot{E}/\dot{E}_p - T(\dot{S}_p - \dot{S})/\dot{E}_p. \quad (30)$$

Since \dot{E}_p is a smoothly varying function (proportional to \dot{N}) whereas \dot{E} may be largely negative and consequently χ largely positive, there is no practical upper bound to χ . On the other hand, the bound on η is finite, i.e. from (25) and (29)

$$\eta \leq 1 - E/E_p - \int_0^t T(\dot{S}_p - \dot{S}) dt'/E_p \equiv \bar{\eta}. \quad (31)$$

Although in practice the rhs of (31) is usually smaller than unity this is not a necessary condition. In principle, if the work producing mechanism tends to increase the entropy of the system (the working substance) heat can be absorbed from the heat bath and released as thermodynamic work without violating the basic laws of thermodynamics. A similar condition prevails for example in electrochemical cells in which the charge transfer reaction is exo-entropic. More generally, (for systems at constant temperature) this is always the case for thermodynamic changes characterized by $|\Delta A| \geq |\Delta E|$.

3. Results and analysis

The time evolution of the thermodynamic functions characterizing the laser system depends on the kinetic scheme, i.e. the combination of rate processes taking place in the laser cavity. In order to elucidate the thermodynamic aspects of specific rate processes we shall examine the behaviour of the HF system under different kinetic schemes. As in paper I this will be achieved by varying the initial conditions or by artificially switching off or on different kinetic factors. In order to relate the kinetic and thermodynamic analyses we shall test, with minor variations, the same kinetic schemes of paper I. In this section we present the results of the time dependent thermodynamic analysis, emphasize the thermodynamic characteristics of specific kinetic schemes and derive several preliminary conclusions. A more general interpretation of the results will be provided in the next section.

Using the labelling and notation of the kinetic analysis [8] the following runs (kinetic schemes, computer experiments) will be analyzed: 1, 3, 4, 5, 6, 7 and 10. Run 2 which is very similar to 1 and runs 8, 9 and 11 which test specific vibrational deactivation routes will be omitted. On the other hand, a new kinetic scheme, no. 12 below, will be included in the analysis. For the sake of convenience, let us briefly outline the features of the relevant kinetic schemes:

(1) "standard". The initial conditions in this run simulate those employed in the experiments of Berry [9]; i.e. the initial gas pressures are $H_2 : CF_3I : Ar = 1 : 1 : 50$ torr. The high inert gas pressure ensures nearly instantaneous rotational equilibration.

(3) " $P_{Ar} = 5$ torr". This run differs from 1 only in the Ar pressure. This leads to lower R-T rates and higher temperature rise.

(4) " $P_{Ar} = 0$ torr". Here rotational energy transfer is slow but not negligible due to the presence of other R-T agents besides Ar.

(5) "Boltzmann". This kinetic scheme ensures rotational equilibrium before, during and after the laser pulse. This was achieved by replacing the experimental nascent rotational distributions of the HF molecules by Boltzmann distributions. In addition, to prevent hole burning effects in the Boltzmann shaped distributions the R-T rate was enhanced by artificially

increasing the R–T rate constants used in 1. The gas mixture was kept as in 1. Note that the initially Boltzmann nascent product distribution has a lower energy content than the real nascent distribution. The difference in the degrees of rotational excitations is $\approx 6\%$ of the pumping reaction exoergicity and $\approx 9\%$ of the total internal excitation (see paper I and below).

(6) “No R–T”. This is the opposite extreme of the former kinetic schemes: i.e. all R–T processes have been eliminated from the kinetic model. The gas mixture and the V–V, T processes are as in 1 and 5.

(7) “No relaxation”. As in 6, but in addition all V–V, T processes have also been eliminated. Since heat transfer is impossible in this kinetic scheme, we shall (sometimes) refer to it as “the frictionless laser”.

(10) “No V–V, T”. This kinetic scheme is identical to the standard one except for the elimination of all vibrational deactivation processes.

Based on the observation [8] that R–T transfer enhances the laser efficiency while V–V, T processes have the opposite effect we have added a run which was not included in the kinetic analysis;

(12) “Boltzmann, no V–V, T”. The kinetic scheme of this laser is identical to that of the Boltzmann laser, no. 5 above, except for the “switching off” of all V–V, T effects.

Detailed time profiles of the thermodynamic functions will be presented for four representative kinetic schemes. Two realistic schemes, the “standard” and the “ $P_{Ar} = 0$ ”, and two synthetic ones, the “no relaxation” (“frictionless”) and “Boltzmann, no V–V, T”. For the other kinetic schemes we shall provide only the integrated values of the thermodynamic functions.

Consider first the results of the “ $P_{Ar} = 0$ ” run which are shown in figs. 1a–1e. The time dependencies of \dot{E}_p and \dot{S}_p are proportional to \dot{N} and those of E_p and S_p to N , cf. eqs. (15)–(18). \dot{Q} is determined primarily by the overall population of excited HF molecules, which is low at early times (when N is low) and becomes considerably higher towards the end of the pulse when the internal energy distribution is nearly constant [8]. (The termination of the laser pulse occurs shortly after \dot{Q} exceeds \dot{E}_p , see below). Therefore, \dot{Q} and Q are slowly varying functions of time. Hence, the lasing characteristics are expected

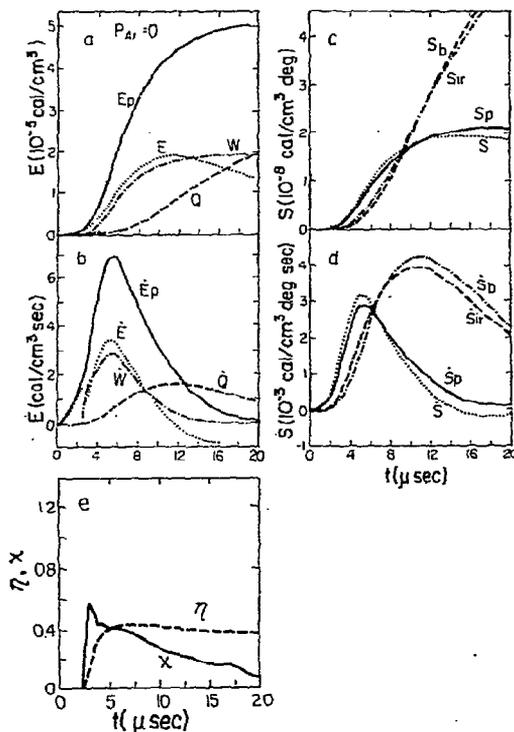


Fig. 1. Time evolution of the thermodynamic functions (per unit volume) of the HF chemical laser for the kinetic scheme “ $P_{Ar} = 0$ ”. (a) The system energy, E , pumping energy, E_p , laser energy (work), W , and the heat transfer to the bath, Q , as functions of time. (b) The time rates of change of E , E_p , W and Q . (c) The system entropy, S , the pumping contribution to the system entropy, S_p , the system contribution to the bath entropy, S_b , and the irreversible entropy, S_{ir} , as functions of time. (d) The time rates of change of S , S_p , S_b and S_{ir} . (e) The instantaneous efficiency χ and the integrated efficiency η as functions of time.

to be exhibited only in the time profiles of \dot{E} , E , \dot{W} , W , \dot{S} , S , the efficiencies χ and η and in certain cases, to be considered below, also in \dot{S}_{ir} and S_{ir} .

Inspection of figs. 1a and 1b reveals that until the lasing threshold, ($t_{th} \approx 2.5$ μsec), $\dot{E} \approx \dot{E}_p$ and $E \approx E_p$. This behaviour is expected since before threshold \dot{Q} and Q are negligible and \dot{W} and W are zero. Thus, below threshold all the energy pumped into the system remains in the internal modes or, in other words, the laser operates as a system with memory. The attainment of threshold is accompanied by a steep increase in \dot{W} and a corresponding decrease in \dot{E} ; $|\dot{E}| < \dot{W}$

since in the $t \approx t_{th}$ region $\dot{Q} \approx 0$ so that $\dot{E}_p \approx \dot{W} + \dot{E} = \dot{W} - |\dot{E}| > 0$. The changes in \dot{W} and \dot{E} are reflected by steep changes in the instantaneous efficiency. Similarly the fast increase of W following the lasing threshold is associated with sudden rise of η . Beyond the threshold region the molecular and photon populations vary slowly [8], in a nearly steady state fashion, and consequently also E , W , S and the efficiencies. The slow decrease of $\eta = W/E_p$ towards the end of the pulse is due to the growing influence of \dot{Q} . After \dot{Q} first exceeds \dot{E}_p , (at $t \approx 13 \mu s$, fig. 1b), the pumping reaction ceases to contribute to the lasing process. The pulse extends somewhat beyond $t = 13 \mu s$ because W can still increase at the expense of the internal energy E . From eq. (1) we see that $\dot{Q} \geq \dot{E}_p$ implies $\dot{W} = -\dot{E} - (\dot{Q} - \dot{E}_p) \leq -\dot{E}$. Fig. 1b confirms that in the region characterized by $\dot{Q} \leq \dot{E}_p$ the internal energy decreases, $\dot{E} \leq 0$. However, the contribution of this region to the total pulse energy is negligible, so practically the pulse terminates shortly after \dot{Q} overcomes \dot{E}_p . Of course, \dot{Q} remains positive also after the laser pulse since the relaxation processes continue to carry the system towards complete thermal equilibrium. The efficiency of the “ $P_{A,r} = 0$ ” system is relatively poor, fig. 1e (see also table 1 below). This is due to the low R–T rates on the one hand and the negative influence of the V–V, T processes on the other hand.

Insights into the lasing mechanism can be gained from the time profiles of the entropy functions and their time rates of change. Before threshold $\dot{S} \approx \dot{S}_p$ and $S \approx S_p$, as expected, figs. 1c and 1d. In the early stages of the pulse, $2.5 \leq t \leq 7 \mu s$, $\dot{S} > \dot{S}_p$ and $\dot{S}_{ir} > \dot{S}_b$. At later times this behaviour is reversed, $\dot{S} < \dot{S}_p$ and $\dot{S}_{ir} < \dot{S}_b$. The inequality $\dot{S}_{ir} > \dot{S}_b$ indicates that there is an additional source for irreversible entropy production in the system, besides the relaxation processes responsible for $\dot{Q} = T\dot{S}_b$. This additional source must be the lasing process itself. Support to this conclusion comes from the inequality $\dot{S} > \dot{S}_p$ which holds when $\dot{S}_{ir} > \dot{S}_b$ and implies that the system entropy increases with a rate faster than that implied by the pumping process alone. Further, more convincing, support is provided by the results for the “frictionless” laser where $\dot{Q} \equiv 0$ but $\dot{S}_{ir} > 0$ (see table 1). In the discussion below we shall argue that $\dot{S} > \dot{S}_p$ and $\dot{S}_{ir} > \dot{S}_b$ are characteristic to lasing under complete vibrational inversion ($N_v > N_{v-1}$) and/or in the ab-

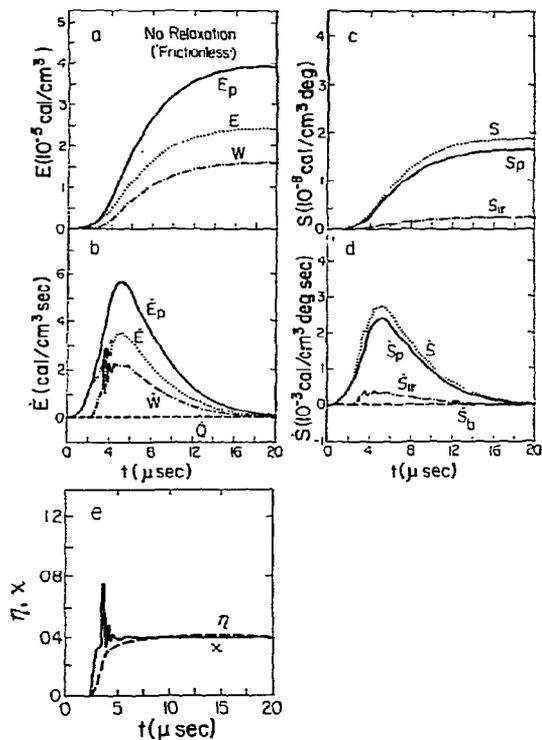


Fig. 2. Time evolution of the thermodynamic functions (per unit volume) of the HF laser system for the kinetic scheme. “No relaxation” (“frictionless”). Other notations as in fig. 1.

sence of efficient rotational relaxation.

The inequality $\dot{S}_{ir} < \dot{S}_b$ which holds at the late stages of the pulse, fig. 1d, indicates that not all the heat transferred to the bath, $\dot{Q} = T\dot{S}_b$, is a dissipated energy, i.e. the positive quantity $\dot{Q}_{rev} \equiv T(\dot{S}_b - \dot{S}_{ir}) > 0$ is constructive for keeping the lasing process in continuation. Anticipating the discussion below, we shall see that this (very small amount) of useful heat production is provided by the rotational relaxation.

The irreversible entropy production in the course of the lasing process is clearly demonstrated in fig. 2 which shows the results for the “frictionless” laser. In this case all the rotational and vibrational relaxation processes have been eliminated from the kinetic model so that \dot{Q} , Q , \dot{S}_b and S_b are identically zero. Hence, $\dot{W} = \dot{E}_p - \dot{E}$, $W = E_p - E$, $\dot{S}_{ir} = \dot{S} - \dot{S}_p$ and $S_{ir} = S - S_p$. Before threshold $W = \dot{W} = \dot{S}_{ir} = S_{ir} = 0$. Clearly, the irreversible entropy production, \dot{S}_{ir} , which starts and decays with the laser pulse is due to

the lasing process. The positive value of $\dot{S} - \dot{S}_p$ throughout the laser pulse confirms our earlier statement that in the absence of rotational energy transfer the lasing process necessarily increases the entropy of the system. Despite the absence of vibrational deactivation the efficiency of the frictionless laser is poor, fig. 2e and table 1. This is due to the absence of a mechanism, i.e. R-T transfer, which could couple the different lasing lines. One may thus generalize the findings for the "frictionless" laser by saying that the complete lack of relaxation processes does not guarantee high efficiency. Certain relaxation processes, though possibly leading to some dissipative losses, may support the useful, work producing, mechanism.

An extremely opposite behaviour to the "frictionless" laser is displayed by the "Boltzmann, no V-V, T" system, fig. 3. Both kinetic schemes do not involve V-V, T processes but the latter is governed by instantaneous rotational relaxation. Here $S_p > \dot{S}$ and $\dot{S}_b > \dot{S}_{ir}$ throughout the lasing; except for a negligibly short time interval in the threshold region, reflecting the passage from complete to partial vibrational inversion [8]. The rate of heat transfer to the bath is very low and is nonzero only during the laser pulse. This is because the only mechanism of heat transfer is rotational relaxation. The role of this mechanism is to prevent hole burning effects in the boltzmannian rotational distributions as a result of the radiative processes. As will be shown in the next section, this involves very little, in fact negligible, energy dissipation. It should be noted, however, that even this small amount of heat transfer $\dot{Q} = T\dot{S}_b$ is, in principle, an avoidable loss since \dot{S}_b is mostly irreversible entropy production; $\dot{S}_b \approx \dot{S}_{ir}$, fig. 3d. The decline of \dot{S}_b towards the end of the pulse confirms that heat exchange with the bath accompanies the stimulated emission processes and ceases afterwards.

The pronounced oscillations in \dot{W} , \dot{E} and χ (which in this case exceeds unity) result from the cooperative mechanism dominating the lasing at rotational equilibrium. Due to the strong coupling between the rotational levels, lasing in each of the vibrational bands occurs almost exclusively on the line with the highest gain. As lasing proceeds the vibrational population ratios N_v/N_{v-1} tend to decrease [8] and the highest gain transition is gradually shifted towards

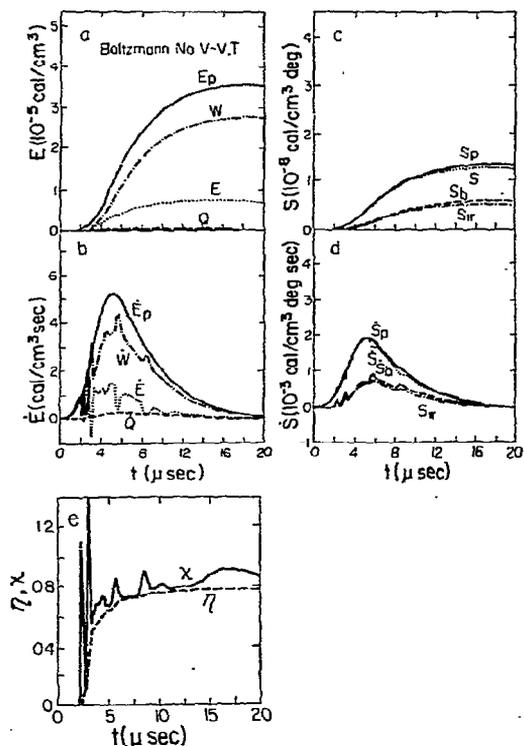


Fig. 3. Time evolution of the thermodynamic functions (per unit volume) of the HF laser for the kinetic scheme "Boltzmann, no V-V, T". Other notations as in fig. 1.

higher J values. The efficient rotational energy transfer supports the pumping reaction in supplying molecules to the lasing transition, thereby enhancing the stimulated emission in the (single) lasing line. The enhanced pumping and stimulated emission are exhibited by the steep variations in \dot{W} and \dot{Q} . The peak structure of these functions reflects the attainment of thresholds on new lines as a result of the J -shifting mechanism. More precisely, the oscillatory patterns of \dot{W} , \dot{Q} and χ represent the superposition of nearly single lasing lines from different vibrational bands.

In both the "Boltzmann no V-V, T" and the "frictionless" lasers the integrated efficiency $\eta = W/E_p$ approaches a constant value, cf. fig. 2e and 3e. After the pulse has terminated E remains constant since there are no relaxation processes. Since E_p also approaches a constant value $\eta = 1 - E/E_p \rightarrow$ constant. Of course, the efficiency of the rotationally equilibrated laser is much higher. Two remarks should

be made regarding the efficiency of this laser. First, we note that η does not approach 1 despite the absence of V-T processes. This is because in this nearly ideal system the termination of the laser pulse is determined by the requirement of threshold inversion, $\Delta N \geq \Delta N_{th}$. This requirement sets a lower limit on the vibrational population ratio N_v/N_{v-1} . It can be shown [14] that this limit is inversely proportional to the overall HF concentration, $N(t \rightarrow \infty)$, and the photon lifetime in the cavity τ_p . For the data of our kinetic model [8,14] the final values of N_v/N_{v-1} are of the order of 0.3. Hence, even at the end of the laser pulse considerable energy is still stored in the vibrational degrees of freedom and consequently η approaches a value lower than unity. The second remark concerns the calculation of η for the "Boltzmann, no V-V, T" laser (no. 12) and the Boltzmann laser (no. 5). In these two cases the average internal energy content of the nascent products, cf. eq. (15), does not include the initial rotational excitation of the HF molecules. Thus $\langle \epsilon_p \rangle$ and E_p are lower than in all other cases and the value calculated for η is somewhat larger than that obtained by including the initial rotational excitation. The ratio between the $\langle \epsilon_p \rangle$'s corresponding to rotationally equilibrated and nonequilibrium nascent products is 0.91. This is the factor by which η of the Boltzmannian lasers should be multiplied in order to obtain their chemical efficiencies, η_c .

The last panel of figures, figs. 4a-4e, shows the results for the "standard" run which most closely resembles an experimental laser system [9]. Because of the large excess of buffer gas in this system, rotational relaxation is almost instantaneous and the general behaviour of the thermodynamic functions is similar to that of the "Boltzmann, no V-V, T" laser. The differences are mainly due to the inclusion of vibrational relaxation in the standard laser. This leads to sizeable heat transfer and irreversible entropy production and hence to some reduction in the laser efficiency.

The integrated values of the thermodynamic functions corresponding to the various kinetic schemes are summarized in table 1. Also listed are the quenching times of the laser pulse, t_q , the translational temperature of the mixture at $t = t_q$, $T_f(t_q)$, and the total number of HF molecules produced by the pumping reaction, $N(t \rightarrow \infty)$. Except for runs 3 and 4, where

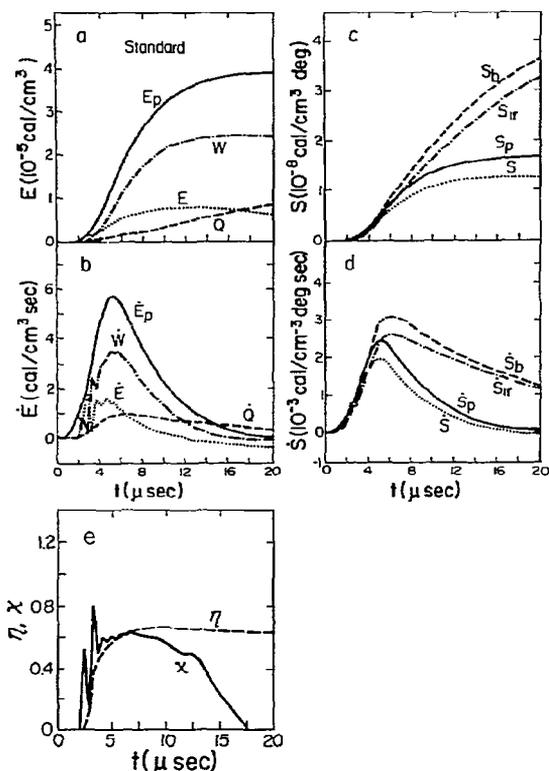


Fig. 4. Time evolution of the thermodynamic functions (per unit volume) of the HF chemical laser for the "standard" kinetic scheme. Other notations as in fig. 1.

the heat capacity of the system is relatively small, the temperature rise is moderated by the larger excess of inert gas. ($T(t=0) = 300$ K in all runs.) According to the kinetic model [8], N and consequently E_p and S_p increase with T_f , as revealed by the results for 3 and 4. The larger number of molecules is also reflected (to different extents) in the other extensive parameters, e.g. W , Q and S but not in the intensive parameters such as $\langle \epsilon_p \rangle$, $\langle \epsilon \rangle$, η , and η_c .

The efficient conversion of internal energy into laser radiation due to the rotational energy transfer processes is reflected by the low values obtained in runs 5 and 12 for the internal energy per molecule at the end of the laser pulse, $\langle \epsilon \rangle(t_q)$. Comparison of $\langle \epsilon \rangle(t_q)$ in the other runs confirms this tendency. The decrease in $\langle \epsilon \rangle$ is accompanied by a decrease in $\langle s \rangle$, the average entropy per molecule. We also note that the higher the R-T rate, the higher is the efficiency of internal energy conversion η , $[\eta(t \rightarrow \infty) = W/E_p(t \rightarrow \infty)]$,

Table 1
Integrated values of thermodynamic functions

| Kinetic scheme | Standard (1) a) | $P_{Ar} = 5$ torr (3) | $P_{Ar} = 0$ (4) | Boltzmann (5) | No R-T (6) | No relaxation ("frictionless") (7) | No V-V, T (10) | Boltzmann no V-V, T (12) |
|--------------------------------|--------------------|--------------------------|---------------------|------------------|---------------|--|-------------------|--------------------------------|
| t_q (μ s) | 15 | 15 | 15 | 15 | 12 | 16 | 17 | 17 |
| T_f (K) | 310 | 352 | 407 | 310 | 310 | 309 | 310 | 310 |
| $E_p(t \rightarrow \infty)$ b) | 3.94 | 4.45 | 4.97 | 3.57 | 3.94 | 3.94 | 3.94 | 3.57 |
| $E_p(t_q)$ | 3.80 | 4.33 | 4.78 | 3.46 | 3.51 | 3.83 | 3.89 | 3.52 |
| $E_p(t_q)$ | 0.77 | 1.11 | 1.70 | 0.73 | 2.03 | 2.37 | 0.80 | 0.75 |
| W | 2.46 | 2.19 | 1.84 | 2.36 | 0.99 | 1.58 | 2.93 | 2.76 |
| $Q(t_q)$ | 0.60 | 1.03 | 1.25 | 0.36 | 0.48 | 0 | 0.23 | 0.03 |
| $S_p(t \rightarrow \infty)$ c) | 1.66 | 1.87 | 2.08 | 1.31 | 1.66 | 1.66 | 1.66 | 1.31 |
| $S_p(t_q)$ | 1.60 | 1.82 | 2.01 | 1.26 | 1.46 | 1.60 | 1.63 | 1.29 |
| $S(t_q)$ | 1.22 | 1.51 | 1.90 | 1.20 | 1.69 | 1.83 | 1.26 | 1.23 |
| $S_b(t_q)$ | 2.89 | 3.61 | 3.75 | 1.63 | 1.69 | 0 | 1.77 | 0.57 |
| $S_{ir}(t_q)$ | 2.51 | 3.30 | 3.64 | 1.57 | 1.92 | 0.23 | 1.40 | 0.51 |
| $N(t \rightarrow \infty)$ d) | 1.51 | 1.71 | 1.91 | 1.51 | 1.51 | 1.51 | 1.51 | 1.51 |
| (ϵ_p) c) | 26.01 | 26.01 | 26.01 | 23.69 | 26.01 | 26.01 | 26.01 | 23.69 |
| (s_p) f) | 10.91 | 10.91 | 10.91 | 8.73 | 10.91 | 10.91 | 10.91 | 8.73 |
| (ϵ) (t_q) e) | 5.14 | 6.65 | 9.25 | 5.09 | 15.00 | 16.06 | 5.34 | 5.03 |
| (s) (t_q) f) | 8.40 | 0.07 | 10.93 | 8.23 | 12.43 | 12.49 | 8.43 | 8.34 |
| $\eta(t \rightarrow \infty)$ | 0.62 | 0.50 | 0.37 | 0.66 | 0.25 | 0.40 | 0.74 | 0.78 |
| η_c | 0.47 | 0.37 | 0.28 | 0.45 | 0.19 | 0.30 | 0.56 | 0.54 |
| $\bar{\eta}(t_q)$ | 0.77 | 0.70 | 0.63 | 0.78 | 0.44 | 0.40 | 0.77 | 0.78 |

a) Indicates run number.

b) E_p , E , W and Q in 10^{-5} cal/cm³ mole. ($W = W(t \rightarrow \infty)$ is somewhat higher than $W(t_q)$ since lasing lasts somewhat beyond the rounded quenching time $-t_q$).

c) S_p , S , S_b and S_{ir} in 10^{-8} cal/cm³ mole deg. d) N in 10^{-9} mole/cm³.

e) (ϵ_p) and (ϵ) in kcal/mole. f) (s_p) and (s) in cal/mole deg.

$W = W(t \rightarrow \infty)$]; compare in particular runs 1 and 5 and 10 and 12. R-T transfer in 5 is somewhat faster than in 1 and in 12 is faster than in 10. Yet, the chemical efficiencies, η_c , of 5 and 12 are slightly lower than those of 1 and 10, respectively. As argued in the kinetic analysis [8] this effect should be attributed to the considerably higher initial rotation excitation of the nascent HF molecules in the kinetic schemes 1 and 5. ($\eta_c = 0.75\eta$ for all runs except 5 and 12, where $\eta_c = 0.69\eta$.) We have also calculated $\bar{\eta}(t_q)$, the thermodynamic bound to the laser efficiency at $t = t_q$, cf. eq. (31). This limit is very nearly reached in two cases. The "frictionless" laser (no. 7) and the "Boltzmann no V-V, T" laser (no. 12). (The differences between η and $\bar{\eta}$ in these cases are negligible.) In the frictionless laser the equality $\eta = \bar{\eta}$ derives from the absence of energy losses by relaxation processes. In the latter case this equality indicates that the

(small) loss of internal energy by rotational relaxation, Q , is essential for the high efficiency of the system. The large differences between the various $\bar{\eta}$ values means that the degree of reversibility of the lasing process (as reflected for example by the ratio $\eta/\bar{\eta}$) is not the major criterion for the efficiency of the laser. Considerably more important is the kinetic scheme itself, i.e. the interplay with the various kinetic processes governing the time evolution of the system. This statement will be given a more rigorous interpretation in the next section.

Finally, it should be noted that in most kinetic schemes the irreversible entropy production is mainly due to dissipative losses by relaxation processes since $S_{ir} \approx S_b$. The irreversible entropy production resulting from the lasing process itself is very small as can be judged from the very low value of S_{ir} obtained for the "frictionless" laser. (Note that S_{ir} in this laser is

identical to the difference $S_{\text{ir}} - S_{\text{b}}$ in the "no R-T" system, where S_{b} stems only from V-T processes. Since R-T processes are absent $S_{\text{ir}} - S_{\text{b}}$ must be the entropy production in the lasing process.) Note also that the absolute value of S_{ir} is very low. That is, even if this amount of irreversible entropy production which (in principle only) could be compensated for by absorbing a quantity of heat $Q = TS_{\text{ir}}$ from the heat bath and converting it into work, the efficiency of the "frictionless" laser would not be improved significantly; $TS_{\text{ir}} = 0.069 \times 10^{-8}$ kcal/cm³ mole $\ll W = 1.58 \times 10^{-8}$ kcal/cm³ mole. Only rotational coupling can improve the laser efficiency, compare runs 7 and 12.

4. Discussion

Disequilibrium is a necessary initial condition which a thermodynamic system must fulfill in order to perform work on external objects. The initial non-equilibrium state is determined by a set of constraints on the system. The most common examples of thermodynamic constraints are thermally (mechanically, chemically) insulating partitions separating between two systems at different temperatures (pressures, chemical potentials). The constraints must not be realized by realistic partitions. More generally, in the statistical (or information theoretic) description of macroscopic molecular systems the constraints are represented by certain requirements imposed on the molecular distribution function. The thermodynamic state of the system is uniquely characterized by the (single) distribution function which maximizes the entropy of the system subject to these requirements [5,7,15,16]. In the context of the present work where the system (by our definition) comprises the internal degrees of freedom of the lasing molecules the constraints apply to the vib-rotational distribution function $P(v, J)$. For example, the formal appearance of the constraints governing $P_i(v, J)$, the nascent products distribution in the reaction $F + H_2 \rightarrow HF(v, J) + H$ is

$$P(v, J) = P_i(v, J) = \text{const.} \quad (\text{every } v, J). \quad (32)$$

In this, fully specified case, maximization of the entropy, eq. (12), (for constant N), yields trivially, $P(v, J) = P_i(v, J)$ and $S = S_p$, cf. eq. (18). On the other

hand, the partially relaxed distribution,

$$P(v, J) = P_i(v)P_B(J|v), \quad (33)$$

where $P_i(v) = \sum_J P_i(v, J)$ is the nascent vibrational distribution, and

$$P_B(J|v) = (2J+1) \exp[-B_v E_J(v)/kT] / q_{\text{rot}}(v, T) \\ \approx (2J+1) \exp[-BJ(J+1)/kT] / q_{\text{rot}}(T), \quad (34)$$

is the Boltzmann rotational distribution in level v , is governed by much fewer constraints; B_v is the rotational constant of level v . The second line in eq. (34) corresponds to the rigid rotor approximation where $B = B_v$ and $E_J(v) = E_J = BJ(J+1)$. q_{rot} is the rotational partition function. The partially relaxed distribution represented by eqs. (33) and (34) is obtained by maximizing S , cf. eq. (12), subject to

$$\sum_J P(v, J) = P(v) = P_i(v) \quad (\text{every } v) \quad (35)$$

and

$$\sum_{v,J} P(v, J) E_J(v) = \langle \epsilon \rangle_R = \text{const.} \quad (36)$$

In the classical rigid rotor approximation, i.e. when $B_v = B$ and $B \ll kT$ (36) is given by

$$\sum_{v,J} P(v, J) E_J = \sum_J P(J) E_J = \langle \epsilon \rangle_R \equiv kT, \quad (37)$$

where T is the heat bath temperature. Hence, the multitude of vib-rotational constraints (32) has been replaced by a few constraints on the vibrational populations, eq. (35), and a single constraint, eqs. (36) or (37), on the rotational populations. (In addition to the physical constraints all distributions must fulfill the normalization constraints.)

Removal of constraints leads to a reduction in the disequilibrium character of the system. More rigorously, according to the second law of thermodynamics, uncontrolled removal of one or more constraints initiates a spontaneous relaxation process. During this process the entropy of the "universe" (the system plus its surrounding) increases until it reaches a maximal value. The state of the system in the new, final, state is uniquely determined by the distribution which maximizes the entropy of the system subject to the surviving constraints; i.e. those left after removing some of the original ones. It could be remem-

bered that it is the total entropy, not the entropy of the system itself, which increases during the relaxation process. For example, the passage from the initial state, eq. (32), to the rotationally relaxed state, eq. (33), involves a decrease in the entropy of the system S . This is reflected by the lower value of S_p in the boltzmannian kinetic schemes, as compared to S_p in all other cases where $P_i(v, J) = P_i(v)P_i(J|v)$. In general, when the system is coupled to a heat bath at temperature T , the removal of constraints is associated with an increase of the "entropy deficiency" [15–17] (or "information content") $TDS[P_i|P_f]$, where P_i and P_f are the initial and final distributions, respectively [5,7,15–17]. The definition of $DS[P_i|P_f]$, for a system containing a fixed number of molecules N , is

$$DS[P_i|P_f] = Nk \sum_n P_i(n) \ln [P_i(n)/P_f(n)], \quad (38)$$

where the sum extends over all the molecular quantum states. $DS[P_i|P_f] \geq 0$; the equality holds if and only if $P_i(n) = P_f(n)$ for all n . If the final state corresponds to complete equilibrium, i.e. $P_i(n) \propto \exp(-E_n/kT)$ then $TDS[P_i|P_f] = -\Delta A_{i \rightarrow f}$, the change in the Helmholtz free energy of the system in the transition $i \rightarrow f$. For the passage from the nascent distribution (32) to the rotationally relaxed distribution (33), eq. (38) yields

$$TDS[P_i|P_f] = NkT \sum_v P(v) \sum_J P_i(J|v) \times \ln [P_f(J|v)/P_B(J|v)]. \quad (39)$$

By controlling the removal of constraints (in analogy to expansion against external pressure), part of the energy of the system and its surrounding can be converted into thermodynamic work. The maximal work, \bar{W} , is obtained when the net (system + surrounding) change of entropy is zero, i.e. in a reversible process [5,15]. It can be shown that $\bar{W}_{i \rightarrow f} = TDS[P_i|P_f]$, cf. eq. (38). Thus, if there was a mechanism which could utilize the initial rotational energy of the nascent products the maximal possible work would be given by eq. (39). (For example, at least part of the initial rotational excitation could be converted into laser radiation if by appropriate choice of gratings the system was forced to lase on pure rotational transitions.) In our case such a mechanism does not

exist and the initial rotational excitation is treated as an unavoidable dissipative loss. More precisely, in our kinetic–thermodynamic description rotational relaxation occurs spontaneously, on a time scale of $\tau_{R-T} \approx 1/k_{R-T}[M]$, where k_{R-T} is the R–T rate constant and $[M]$ the total gas density. In the kinetic schemes corresponding to high inert gas pressures, e.g. in the standard case, τ_{R-T} is typically very short, $\approx 10^{-8}$ s, except for high J levels, where k_{R-T} is small. The boltzmannian kinetic schemes correspond to $k_{R-T} \rightarrow \infty$ which implies $\tau_{R-T} \rightarrow 0$. Thus, in the boltzmannian schemes it was a priori assumed that the initial rotational excitation is given to the bath and practically so also in the high pressure schemes. In the latter cases this involves a positive contribution to Q , S_b and S_{ir} . On the other hand, in the "no relaxation" ("frictionless") or the "no R–T" lasers, where $k_{R-T} \equiv 0$ and thus $\tau_{R-T} \equiv \infty$, there is no energy loss and consequently no heat and irreversible entropy production due to rotational relaxation. In particular, among all the kinetic schemes, the "frictionless" laser is the one which involves the least amount of irreversible entropy production, see table 1. Nevertheless, the amount of work produced by this laser is considerably lower than that obtained in the boltzmannian, the standard and the "no V–V, T" lasers despite the loss of the nascent rotational energy and the higher S_{ir} values in these cases. Hence, the number and character of the constraints governing the system throughout the lasing, and not the reversibility of the process is the major criterion for the laser efficiency.

To clarify the origin and the consequences of the last statement, let us compare two representative cases: The "frictionless" and the "no V–V, T" schemes. Both cases are characterized by the same initial state, $P_i(v, J)$, and in both the effects of vibrational relaxation have been eliminated. The two schemes differ only in the extent of rotational relaxation. (This is also the only difference between the "standard" and the "no R–T" schemes.) The constraints on the final state which characterize the system at the end of the work production period depend on the interaction between different parts of the system and between the system and the heat bath. In the "frictionless" laser $P(v, J) = P_i(v, J)$ until threshold is reached. The start of lasing involves removal of constraints from the initial distribution. Due to

the absence of collisional energy transfer processes the variations in $P(v, J)$ are only a result of the lasing process itself which we have limited to P-branch, $v, J - 1 \rightarrow v - 1, J$, transitions. Hence, during and at the end of the laser pulse the distribution function must fulfill the conditions

$$\sum_v P(v, J - v) = \sum_v P_i(v, J - v) = P(g_j) = \text{const.}, \quad (40)$$

where g_j denotes the group of levels connected by consecutive P-branch transitions; e.g. the levels $v, J = 3, 2; 2, 3; 1, 4$ and $0, 5$ constitute one such group.

On the other hand, in the "no V-V, T" laser where rotational energy transfer is very fast, molecules are rapidly exchanging their J number. Consequently, instead of the numerous constraints (40) the only condition imposed on $P(v, J)$ is (36). It is not difficult to show [5] that the single constraint (36) can be expressed as a linear combination of the constraints (40). More generally, it can be shown [5] that if an initial state i governed by n constraints can develop into two different final states f and f' governed by $m < n$ and $m' < m < n$ constraints, respectively, such that the m' constraints are linear combinations of the m constraints, then $\bar{W}_{i \rightarrow f'} > \bar{W}_{i \rightarrow f}$ and $\bar{W}_{i \rightarrow f} = \bar{W}_{i \rightarrow f'} + \bar{W}_{f' \rightarrow f}$. This provides a qualitative explanation for the pronounced superiority of the "no V-V, T" scheme over the "frictionless" scheme. From table 1 we see that although the actual work obtained in the first case does not reach its maximal possible value (as reflected by $\bar{\eta} > \eta$) because of some dissipative losses, it is by far larger than the work extracted from the "frictionless" laser.

Both the "frictionless" and the "no V-V, T" laser types involve some irreversible entropy production. Yet, the origins of \dot{S}_{ir} in these two cases are different and should be explained. This explanation will also shed light on the large quantitative difference in the corresponding efficiencies and facilitate the analysis of the other kinetic schemes. The pumping characteristics, \dot{E}_p and \dot{S}_p , are the same in both kinetic schemes. Therefore, in order to sharpen the differences, we shall eliminate the effects of pumping by considering the behaviour of the system subject only to the lasing and rotational relaxation processes. Specifically, let us consider the conditions on $P(v, J)$ and the changes in the thermodynamic functions of a system containing N molecules following

an infinitesimal amount of lasing in some P-branch transition, $v, J - 1 \rightarrow v - 1, J$. The description below can be extended to include the effects of pumping and simultaneous lasing on many lines. However, this involves lengthy derivations and explanations which do not provide additional physical insights. We shall therefore discuss only the specific situation just described.

Consider first the "frictionless laser". The change, per unit time, in $P(v, J)$ following the passage of $N\dot{P}(v, J - 1)$ molecules from level $v, J - 1$ to $v - 1, J$ is found by setting $\dot{P}(v - 1, J) = -\dot{P}(v, J - 1) > 0$, and $\dot{P}(v', J') = 0$ for all $v', J' \neq v, J - 1$ or $v - 1, J$. The corresponding changes in the internal energy and entropy of the system are, [set $\dot{N} = 0$ in eqs. (11) and (13)],

$$\begin{aligned} \dot{E}(v, J - 1 \rightarrow v - 1, J) &= -\dot{W}(v, J - 1 \rightarrow v - 1, J) \\ &= N\dot{P}(v - 1, J)(E_{v-1, J} - E_{v, J-1}) \\ &\approx -N\dot{P}(v - 1, J)(\hbar\omega - 2BJ), \end{aligned} \quad (41)$$

$$\begin{aligned} \dot{S}(v, J - 1 \rightarrow v - 1, J) &= \dot{S}_{ir}(v, J - 1 \rightarrow v - 1, J) \\ &= Nk\dot{P}(v - 1, J) \ln \left[\frac{P(v, J - 1)/P(v - 1, J)}{(2J - 1)/(2J + 1)} \right], \end{aligned} \quad (42)$$

where the second equality in (41) corresponds to the rigid rotor-harmonic oscillator (RRHO) approximation; $E_{v, J} = E_v + E_J(v) \approx E_v + E_J = \hbar\omega(v + \frac{1}{2}) + BJ(J + 1)$. In eqs. (41) and (42) we have identified $\dot{W} = -\dot{E}$ and $\dot{S}_{ir} = \dot{S}$, as implied by the absence of pumping and relaxation processes. Eq. (41) expresses the fact that the passage of $N\dot{P}(v, J - 1)$ molecules (per unit time) from $v, J - 1$ to $v - 1, J$ involves the release of an equivalent number of photons with frequency $\hbar\omega - 2BJ$. This process must be accompanied by a positive entropy change of the system, i.e. the r.h.s. of eq. (42) must be positive. That is, $P(v, J - 1)/(2J - 1) > P(v - 1, J)/(2J + 1)$ is a necessary lasing condition. This is, of course, the familiar requirement for positive population inversion. The irreversible entropy production in the "frictionless" laser is thus an inherent consequence of the lasing mechanism. Eq. (42) also implies that lasing in $v, J - 1 \rightarrow v - 1, J$ terminates with $P_f(v, J - 1)/(2J - 1) = P_f(v - 1, J)/(2J + 1)$, i.e. when the (degeneracy averaged) populations become equal. The same arguments apply to all the v, J levels associated with lasing transitions. Summation over all J 's reveals that $P_f(v) \approx P_f(v - 1)$.

This explains the high entropy and energy contents of the system at the end of the lasing. The small absolute magnitude of \dot{S}_{ir} is due to the fact that entropy changes associated with vibrational and rotational degrees of freedom are always small [6].

Consider now the “no V–V, T” case. Here rotational relaxation is nearly instantaneous so that at every moment $P(v, J) = P(v)P_{\text{B}}(J|v)$, where $P_{\text{B}}(J|v)$ is the Boltzmann distribution, eq. (34). The lasing on $v, J-1 \rightarrow v-1, J$ tends to burn a hole in $v, J-1$ and create a hump in $v-1, J$. However, the fast rotational relaxation restores immediately the Boltzmannian shapes of the rotational distributions in the upper and lower vibrational manifolds. Hence, the transfer of $N\dot{P}(v-1, J) = -N\dot{P}(v, J-1) = N\dot{P}(v)P_{\text{B}}(J-1|v)$ molecules (per unit time) via the radiative transition, which implies

$$\begin{aligned} \dot{W}(v, J-1 \rightarrow v-1, J) &= -N\dot{P}(v)P_{\text{B}}(J-1|v)(E_{v, J-1} - E_{v-1, J}) \\ &\approx -N\dot{P}(v)P_{\text{B}}(J-1)(\hbar\omega - 2BJ), \end{aligned} \quad (43)$$

is accompanied by heat transfer to the bath given by

$$\begin{aligned} \dot{Q}(J \rightarrow J-1) &= -N\dot{P}(v)P_{\text{B}}(J-1|v)[E_J(v-1) - E_{J-1}(v)] \\ &\approx -N\dot{P}(v)P_{\text{B}}(J-1)2BJ. \end{aligned} \quad (44)$$

The third lines in (43) and (44) correspond to the RRHO approximation. $\dot{Q}(J \rightarrow J-1)$ is the net amount of energy released by R–T transfer to the bath in order to maintain the average rotational energy per molecule, eq. (37), constant. That is, $2BJ$ is the heat transfer to the bath following the release of a photon with frequency $\hbar\omega - 2BJ$. Clearly, the net change in the energy of the system is

$$\begin{aligned} \dot{E}(v \rightarrow v-1; J) &\equiv -\dot{W}(v, J-1 \rightarrow v-1, J) - \dot{Q}(J \rightarrow J-1) \\ &= N\dot{P}(v)P_{\text{B}}(J-1|v)(E_v - E_{v-1}) \approx \dot{P}(v)P_{\text{B}}(J-1)\hbar\omega, \end{aligned} \quad (45)$$

where, again, the last equality is for the RRHO level scheme. Eq. (45) indicates that the net result of the lasing and rotational relaxation is a decrease in the vibrational energy of the system. The decrease by the amount $\hbar\omega$ per molecule per unit time, is divided between the radiation, $\hbar\omega - 2BJ$, and the heat bath, $2BJ$. Since $2BJ \ll \hbar\omega$, $\dot{Q} \ll \dot{W}$ and most of the energy

is released in the useful channel.

The net change in the entropy of the system corresponding to the energy change (45) is obtained from $\dot{S} = -Nk\Sigma\dot{P}(v, J)\ln[P(v, J)/2J+1]$, [see eq. (13), $\dot{N} = 0$], by setting $\dot{P}(v, J) = \dot{P}(v)P_{\text{B}}(J|v)$, $\dot{P}(v-1) = -\dot{P}(v)$ and $\dot{P}(v') = 0$ for all $v' \neq v$ and $v-1$. The result, in the RRHO approximation, is

$$\dot{S}(v \rightarrow v-1; J) = -Nk\dot{P}(v)P_{\text{B}}(J-1)\ln[P(v)/P(v-1)]. \quad (46)$$

The entropy change of the bath is (RRHO)

$$\dot{S}_{\text{b}}(J \rightarrow J-1) = \dot{Q}(J \rightarrow J-1) = -N\dot{P}(v)P_{\text{B}}(J-1)2BJ/T. \quad (47)$$

The net entropy production in the system and the bath must be non-negative. Hence

$$\begin{aligned} \dot{S}_{\text{ir}}(v \rightarrow v-1; J) &= \dot{S}(v \rightarrow v-1; J) + \dot{S}_{\text{b}}(J \rightarrow J-1) \\ &= -Nk\dot{P}(v)P_{\text{B}}(J-1)\left[\ln\frac{P(v)}{P(v-1)} + \frac{2BJ}{kT}\right] \geq 0. \end{aligned} \quad (48)$$

Since $\dot{W} \geq 0$ requires $\dot{P}(v) < 0$, cf. eq. (43), we find from (48) that

$$J \geq \frac{kT}{2B} \ln \frac{P(v-1)}{P(v)}, \quad (49)$$

which is the familiar lasing condition on P-branch transitions at rotational equilibrium [1–12]. The high efficiency of the rotationally equilibrated lasers is due to the fact that even under partial inversion, $P(v) < P(v-1)$, there are sufficiently high J 's through which lasing can continue to take place. Furthermore, it can be shown that the smallest J satisfying (49) is also the highest gain line, i.e. the nearly single lasing transition at rotational equilibrium [11,13,14]. Hence, at complete rotational equilibrium we expect that \dot{S}_{ir} will be very small (see the results for run 12 in table 1). In fact, $\dot{S}_{\text{ir}} \geq 0$ only because the rhs of eq. (49) is continuous while J is discrete so that \dot{S}_{ir} is finite. It should be noted that the condition $P(v) < P(v-1)$ which practically holds throughout the laser pulse implies $\dot{S} < 0$, see eq. (46). This explains the reduction in the system entropy (as reflected by $\langle s_{\text{p}} \rangle \geq \langle s \rangle$) in all the kinetic schemes governed by fast rotational relaxation. The entropy decrease of the system is compensated for by the entropy increase of the bath, \dot{S}_{b} . The high efficiency of these schemes is due to the fact that lasing can continue and terminate

with low $P(v)/P(v-1)$ values without violating the condition $S_{ir} \geq 0$.

The small amount of S_{ir} associated with maintaining the Boltzmannian shape of the rotational distributions is reflected by the results for run 12 (fig. 3 and table 1). We also note that $S_{ir} \geq S_b$. The inequality $S_{ir} > S_b$ is due to the early stages of the lasing where $P(v) > P(v-1)$ and $|\dot{P}(v)|$ is relatively large. In the "no V-V, T" run both S_{ir} and S_b are larger because of the initial rotational relaxation from $P_i(J)$ to $P_b(J)$ which is not accounted for in the "Boltzmann no V-V, T" run. The larger difference $S_{ir} - S_b$ in the "no V-V, T" run stems from the incomplete rotational relaxation of the high J levels. Similar (small) differences are expected and observed between the "standard" (1), and the "Boltzmann" (5) schemes.

The "standard" and "Boltzmann" schemes differ from the "no V-V, T" and the "Boltzmann no V-V, T" (respectively) only to the extent of vibrational relaxation. This is also the only difference between the kinetic schemes "no R-T" and "no relaxation". Table 1 reveals that in all cases the vibrational relaxation lowers W and η and increases Q , S_b and S_{ir} . This behaviour is expected since the V-V, T processes compete rather than cooperate with the lasing.

5. Concluding remarks

In this paper we presented, to the best of our knowledge, for the first time, a detailed time dependent thermodynamic analysis of a realistic chemical laser system. We attempted to prove that thermodynamic considerations can provide new insights into the behaviour of the nonequilibrium chemical laser systems. The thermodynamic description, by its nature, is less detailed than the kinetic-microscopic description as it concentrates on only few macroscopically significant quantities. The kinetic and thermodynamic points of view are complementary, not alternative, to each other. The principal general conclusion of this paper is that the crucial factor in determining the actual laser efficiency is not the reversibility of the lasing but, rather, the kinetic scheme (the thermodynamic constraints) that this process must fulfill. More specifically, it was shown, based on thermodynamic considerations, why and to what extent rotational relaxation enhances the efficiency

and vibrational relaxation reduces the efficiency of the laser.

Since the time dependent thermodynamic approach described in this paper is based on the results of the kinetic analysis, it is an analytic or reformulative rather than a predictive approach. As mentioned above, its main virtue is to condense the very detailed kinetic data into a few macroscopic quantities of thermodynamic interest. Moreover, the time independent thermodynamic description, which can be regarded as a special case of the time-dependent one, does provide upper bounds to the laser efficiency for various conditions [5,6] and thus serves as a partially predictive tool. It is desirable of course that actual efficiencies could also be predicted; a goal which, hopefully, will also be achieved.

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